

990,273



PATENT SPECIFICATION

NO DRAWINGS

990,273

Date of Application and filing Complete Specification: May 3, 1961.

No. 15967/61.

Application made in United States of America (No. 26408) on May 3, 1960.

Complete Specification Published: April 28, 1965.

© Crown Copyright 1965.

Index at acceptance:—C3 P (7A, 7C3, 7D1A, 7FX, 7T2B, 7T2C, 7T2X, 12); B2 E1A

Int. Cl.:—C 08 f // D 21 h

COMPLETE SPECIFICATION

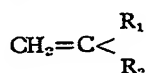
Method of Modifying the Properties of Polyethylene and the Resulting Products

- We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester 4, New York, United States of America, (assignee of HARRY WESLEY COOVER, JR., MARVIN ANTHONY MCCALL and JAMES EDWIN GUILLET) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a method of modifying the properties of polyethylene and to the resulting products. The principal object of the invention is to increase the value and versatility of polyethylene and we have found that this can be accomplished by thermally treating it in the presence of a polymer which serves as a modifier.
- Many methods have been developed for the preparation of polymeric products having properties adapting them to a specific use. For example, previous attempts have been made to "customize" or "tailor" polyethylene, i.e. to import certain properties to polyethylene to adapt it to particular uses, by such methods as polymerization control, copolymerization, cracking, blending, compounding, cross-linking and powdering. However, there is still need for a method for the preparation and separation from polyethylene of polymers having the desired combination of characteristics.
- It is known that polymeric materials can be degraded thermally at temperatures above about 250° C. into lower molecular weight materials. We have now found that when polyethylene is degraded by heating it to a temperature of at least 260° C. in admixture with a polymer of another α -olefinic compound, a polymeric product having useful and unexpected properties is obtained.
- It is well known that high molecular weight polyethylene has many desirable properties which make it useful as a moulding and coating material. For many applications, however, high molecular weight polyethylene has certain undesirable properties which limit its usefulness. For example, considerable difficulty is encountered in printing or dyeing polyethylene; also considerable difficulty is often encountered because polyethylene does not adhere to certain material as well as is desired. It is also known that polyethylene is not very compatible with many resins, waxes, oils and additives used in many coating operations and in many wax and grease formulations, thus limiting its use. In addition, in the paper coating industry considerable difficulty is encountered as a result of the high viscosity of molten polyethylene. However, the present invention now provides new thermally modified polymers and a method for their production which substantially overcome these aforementioned difficulties.
- According to the present invention, there is provided a method of modifying the properties of polyethylene which comprises heating at a temperature of at least 260° C. for at least one minute, a mixture of polyethylene having a density of at least 0.91 and a molecular weight of at least 10,000, with an amount from one-twentieth to nineteen times its weight of a modifier which consists of at least one homopolymer or copolymer derived from one or more polymerizable organic compounds containing, or each containing, at least one $\text{CH}_2=\text{C}<$ group, other than ethylene alone whereby the temperature and time of heating are sufficient to degrade the polyethylene and effect reaction between the polyethylene and the modifier.
- In this specification the molecular weights were determined by the inherent viscosity in accordance with P. W. Allen, Techniques of Polymer Characterization, Academic Press, New York, 1959, page 173.
- All references throughout this specification

[Pri.]

to densities are to conditional densities determined in a density gradient tube as described hereinafter.

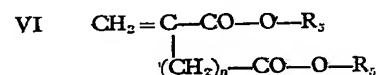
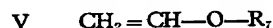
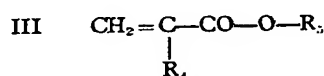
- 5 The homopolymer or copolymer may be derived from one or more polymerizable organic compounds of the general formula:



I
wherein either

- 10 R_1 represents a methyl group and R_2 represents an aliphatic, ethylenically unsaturated aliphatic or aromatic hydrocarbon radical containing from 1 to 20 carbon atoms, or

- 15 R_1 and R_2 together represent the group $=\text{CH}_2$ or $=\text{CHR}_3$ where R_3 is an alkyl group. Most suitably, the homopolymer or copolymer is derived from one or more unsaturated polymerizable organic compounds of any of the general formulae:—



25 wherein

R_3 represents an aliphatic, ethylenically unsaturated aliphatic or aromatic hydrocarbon radical containing from 1 to 20 carbon atoms,

- 30 R_4 represents a hydrogen atom or a methyl group,

R_5 represents an alkyl group containing from 1 to 8 carbon atoms,

- 35 R_6 represents a hydrogen atom, an aryl group, a methyl group, a halogenomethyl group or an alkoxyethyl group in which the alkoxy radical contains from 1 to 8 carbon atoms,

- 40 R_7 represents an alkyl group containing from 1 to 8 carbon atoms, an alkenyl or aralkenyl group containing from 1 to 8 carbon atoms, an alkoxyalkyl group containing from 1 to 8 carbon atoms in its alkyl and alkylene residues or a halogenoalkyl group containing from 1 to 8 carbon atoms, and

n represents 0 or 1.

- 45 The heating may be carried out at a temperature within the range 260° to 450° C. and is preferably carried out at a temperature within the range 290° to 400° C.

- 50 Most suitably, the time of heating does not exceed 4 hours.

The heating is preferably carried out in the absence of air.

The preferred modifiers are polypropylene, polystyrene, polymethyl methacrylate, poly-3-methylbutene-1, and the copolymer of 4% 55 butene-1 with 96% ethylene, by weight.

The invention includes the products obtained by the methods of the invention.

In carrying out the present invention a mixture comprising from 5 to 95% by weight, of 60 polyethylene and from 95 to 5% of a modifying polymer, as defined above, is preferably heated at a temperature within the range of 260° to 450° C., most suitably within the range 290° to 400° C., for a time from one 65 minute to 4 hours, but longer periods may be desirable in some cases. The resulting polymeric products have improved clarity, tensile strength, elongation, grease and oil resistance, dyeability of fibres, as well as many other 70 desirable characteristics.

Any relative proportions of polyethylene and of a modifying polymer within the ranges defined above, can be used in the practice of this invention, rendering it possible to modify the 75 properties of polyethylene in many different ways. Such a process of thermal treatment allows the polyethylene to be "tailored" for many new and specific uses that were not possible using polyethylene alone or mixtures of 80 polyethylene with other polymers or of conventional copolymers of the same composition. The properties of the thermally modified polymers obtained by the method of the present invention are different from those of a single 85 ethylene polymer which has been thermally degraded to the same degree. The properties are also different from those of mechanical mixtures of the two thermally degraded polymers and from copolymers having the same 90 over-all composition. Hence, many properties of polyethylene such as hardness and softening point may be either increased or decreased simply by judiciously choosing the right combination of polymeric materials to be thermally 95 treated.

The thermally modified polymers obtained by the method of the present invention exhibit the improved properties indicated above, but in addition, the compatibility of these new 100 thermally modified polymers with paraffin, oils, resins, soaps and the like, is generally better than that of the unmodified polymers. For example, the cloud point (which is a measure of compatibility of the polymer in paraffin 105 mixtures) is considerably lower with the thermally modified polymers than with unmodified polyethylene or a simple mechanical mixture of polyethylene with the same modifying polymer. Moreover, it is possible to form waxes 110 which are emulsifiable by merely making a proper choice of modifier. This is a very valuable result since, prior to this invention, it was thought necessary to degrade and then oxidize polyethylene to form an emulsifiable wax. Furthermore, the properties of the new thermally 115 modified polymers are different from those


5 obtained by simple mechanical blending or from conventional copolymers of the same overall composition. In general, these new products have higher melting points than copolymers of similar composition and also show improved flexibility and/or less crazing as compared with mixtures having the same percentage composition.

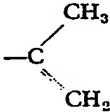

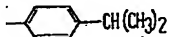

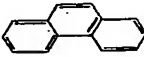
10 Those thermally modified polymers obtained by the method of the invention which are low molecular weight waxes can be used to coat paper to produce a coated material with improved heat sealing properties due to a lowering of the embrittlement tendency possessed by conventional polyethylene waxes or mechanical mixtures of polyethylene wax with paraf-

fin or other natural waxes. Hence, these new low molecular weight thermally modified polymers are useful as substituted for more expensive vegetable and mineral waxes, as additives to other waxes, polymers and greases, as coating materials for paper, cloth, wood, metal and as synthetic materials.


20 Among the polymeric modifiers which may be used in the invention are polypropylene and those derived from one or more ethylenically unsaturated polymerizable monomers such as vinyl esters, vinyl ethers, α - β - unsaturated acid esters, olefins, acrylates, methacrylates, methylenemalonates and itaconates. These are exemplified in the following Table I.


TABLE I

Monomer	Formula 1	
	R ₁	R ₂
Iso-butene	-CH ₃	-CH ₃
2,3-Dimethylbutadiene	-CH ₃	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C} \\ \\ \text{CH}_2 \end{array}$
α -Methylstyrene	-CH ₃	
Allene	=CH ₂	
Butadiene-1,2	=CH-CH ₃	
Pentadiene-1,2	=CH-CH ₂ -CH ₃	
Neopentylbutadiene-1,2	=CH-CH ₂ -CH ₂ -C(CH ₃) ₃	

Monomer	R ₃ in Formula II
Butene—1	$-\text{CH}_2-\text{CH}_3$
3—Methylbutene—1	$-\text{CH}(\text{CH}_3)_2$
3—Methylpentene—1	$-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$
Hexene—1	$-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$
Heptene—1	$-\text{CH}_2(\text{CH}_2)_3-\text{CH}_3$
Dodecene—1	$-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$
Pentadiene—1,3	$-\text{CH}=\text{CH}-\text{CH}_3$
Pentadiene—1,4	$-\text{CH}_2-\text{CH}=\text{CH}_2$
Isoprene	
Neopentylbutadiene—1,3	$-\text{CH}=\text{CH}-\text{CH}_2-\text{C}(\text{CH}_3)_3$
Hexadiene—1,3	$-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
Styrene	
<i>p</i> —Isopropylstyrene	
Octadecene—1	$-\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$
Vinylnaphthalene (α or β)	
Vinylphenanthrene	

Monomer	Formula III	
	R_4	R_5
n-Butyl acrylate	H	$-\text{CH}-(\text{CH}_2)_2-\text{CH}_3$
Isopropyl acrylate	H	$-\text{CH}(\text{CH}_3)_2$
Methyl methacrylate	CH_3	CH_3
t-Butyl methacrylate	CH_3	$-\text{C}(\text{CH}_3)_3$

Monomer	R_5 in Formula IV
Vinyl acetate	$-\text{CH}_3$
Vinyl monochloroacetate	$-\text{CH}_2\text{Cl}$
Vinyl methoxyacetate	$-\text{CH}_2\text{OCH}_3$
Vinyl benzoate	

Monomer	R_6 in Formula V
Vinyl methyl ether	$-\text{CH}_3$
Vinyl ethyl ether	$-\text{CH}_2-\text{CH}_3$
Vinyl propyl ether	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Vinyl isopropyl ether	$-\text{CH}(\text{CH}_3)_2$
Vinyl n-butyl ether	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Vinyl isobutyl ether	$-\text{CH}_2-\text{CH}(\text{CH}_3)_2$
Vinyl t-butyl ether	$-\text{C}(\text{CH}_3)_3$
Vinyl 2-ethylhexyl ether	$-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-(\text{CH}_2)_3-\text{CH}_3$
Vinyl 2-methoxyethyl ether	$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$
Vinyl 2-chloroethyl ether	$-\text{CH}_2-\text{CH}_2\text{Cl}$
Vinyl allyl ether	$-\text{CH}_2-\text{CH}=\text{CH}_2$
Vinyl styryl ether	$-\text{CH}=\text{CH}-$ 

Monomer	Formula VI	
	R_5	n
Diethyl methylenemalonate	C_2H_5	0
Diethyl itaconate	C_2H_5	1

The polymeric modifiers which can be used in the practice of this invention are quite numerous and represent a wide variety of different materials. The most satisfactory modifiers are those characterized by a molecular weight of at least 10,000 and a density in the range of 0.8 to 1.8.

The ethylene homopolymers used as starting materials in the practice of this invention include conventional polyethylene as well as high-density polyethylene and are preferably those having a density in the range of 0.91 to 0.97 and an inherent viscosity of at least 0.7.

The characteristics of the new thermally modified polymers obtained by the process of the present invention can be varied over a wide range and will, to a large extent, be determined by the conditions of treatment as well as by the particular starting materials employed. In general, however, the products obtained will range from waxes with molecular weights as low as 500 to rigid plastics having molecular weights of 100,000 or higher. Accordingly, the inherent viscosities can range from 0.1 or less to 3.0 or more. The densities of the products will depend upon the densities of the polyethylene and modifier and, in general, will be slightly greater than the weight average of densities used in the starting mixture before thermal modification.

In carrying out the present invention, it is preferred that the thermal modification be effected in the absence of air. This can be accomplished by carrying out the heating in vacuum or in an inert gas such as nitrogen and the like, in bulk or in the presence of a suitable diluent such as hexane, mineral spirits, benzene, xylene or the like. Excellent results are achieved by heating a mixture comprising 5—95%, or more preferably 50—90%, polyethylene and 95—5%, or 50—10%, of modifying polymer under conditions such that the molecular weight of polyethylene, if heated in the absence of modifier, would be decreased at least 10% and preferably 50% or more. The most suitable time of heating will depend upon such variable factors as the temperature employed, the molecular weights of the polymers employed and the desired characteristics to be achieved. Thus, the molecular weight of the product can be changed by variation in the temperature or time of heating, higher temperatures leading to lower molecular weight

products. Consequently, the time of heating, in any particular case, will depend upon the correlation of the several variable factors.

The method of the present invention can be carried out with conventional equipment, and can be carried out batchwise, or continuously. In a continuous process it is desirable to extrude the mixture of polyethylene and modifier in a conventional extruder into a heated zone where it is maintained at the desired temperature for the requisite time of 1 minute to several hours to achieve the desired degree of modification. Likewise, the heating can be carried out in a flowing stream reactor such as a tubular reactor, if desired, or can be effected in an inert hydrocarbon solvent, either batchwise or in a continuous flowing stream process.

The preparation of typically thermally modified polymers by the method of the invention is illustrated by the following examples, to which the invention is not limited.

EXAMPLE 1

One hundred forty grams of polyethylene (molecular weight 20,000, density 0.916) and 60 grams of polystyrene (molecular weight 50,000, density 1.05) were heated under nitrogen. The temperature was gradually raised from 275° C. to 325° C. and held at this temperature for 4 hours. Some monomeric or low boiling materials were distilled from the reaction mixture. The resulting polymer was dissolved in hot benzene and poured into warm acetone with vigorous stirring and filtered. The solid was redissolved in hot benzene and reprecipitated by mixing the solution with butyl acetate. The remaining solid polymer was separated by filtering. The percent carbon found was 87.0%, and hydrogen was 12.6%, which is approximately the value expected for a composition containing 30% styrene units. Analysis by infra-red indicated the presence of polystyrene groups in the polymer, and the composition was unchanged by successive fractionation, indicating that the thermally modified material was not a simple mechanical mixture. Pure polystyrene is soluble in butyl acetate and would have been removed from the polyethylene by this treatment if present in a simple mechanical mixture. The product was a hard wax having an inherent viscosity of 0.42 in tetralin at 100° C. at a concentration of 0.25 gms./100 cc. The penetration hardness

BEST AVAILABLE COPY

was 2.0 mm. with a 250-gm. weight as compared with 6.3 for a similar polyethylene wax.

EXAMPLE 2

5 Polyethylene (180 gms. I.V. 0.98, molecular weight 22,000, density 0.92) was blended with 20 gms. of poly-3-methyl butene-1 (crystalline m.p. 245° C.) and heated at 300—350° C. under nitrogen over a period of 1 hour. The product had a higher softening point (crystalline m.p. was in the 130—142° C. range) than that of unmodified polyethylene. This higher softening point is a valuable property in polyethylene fibres since higher ironing temperatures can be obtained.

EXAMPLE 3

15 Polyethylene (160 gms. I.V. 0.98, molecular weight 22,000, density 0.92) and polyhexene-1 (40 gms. I.V. 1.5 molecular weight 150,000, density 0.84) were blended together and heated to 180—365° C. for 40 minutes with vigorous stirring. The resulting polymer had an I.V. of 0.7 and much greater flexibility and elongation than the unmodified polyethylene. This increased flexibility was accompanied by a minimum of crazing or blushing whereas when a simple mixture of these materials were prepared the material crazed and blushed badly when flexed. A more detailed showing of the improved combination of properties is set forth in Table 2 which follows.

EXAMPLE 4

35 Polyethylene (200 gms. I.V. 1.8, molecular weight 22,000, density 0.96) was blended on hot rolls with 10 gms. of polyisobutylene (polyisobutene molecular weight 325,000, density 0.86). This thoroughly mixed material was then heated to 350° C. under nitrogen with stirring for 20 minutes. The product had an inherent viscosity of 1.2 and a density of 0.952 and could be injection moulded to give products of improved toughness and flexibility.

EXAMPLE 5

45 Polyethylene (400 gms. I.V. 1.23, molecular weight 38,000, density 0.92) was blended with a copolymer (40 gms. IV 1.4, molecular weight 50,000, density 0.956) containing 4% butene-1 and 96% ethylene. This blend was thermally modified by heating to 320° C. in a 1000-cc., three-neck flask while stirring under 1-mm pressure for 30 minutes. A small amount of volatile material was removed during this operation. The resulting thermally modified polymer had an I.V. of 0.90. The properties of this polymer are contrasted with those of the simple blend in Table 3 which follows.

50 Films of the three resins in Table 3 were extruded from a flat die through a water quench bath situated 1 inch from the die face. The improvement in film transparency and elongation, which is a measure of toughness, illustrates the desirable characteristics of the

thermally modified resin as compared to simple blends of the two components.

EXAMPLE 6

65 Fifteen pounds of cis 1-4-polybutadiene having a molecular weight of 100,000 and a density of 1.01 was blended on hot rolls with 85 lb. of polyethylene having a molecular weight of 38,000, a density of 0.918 and an inherent viscosity of 1.23. (Cis-1-4-polybutadiene is a polymer of 1,3-butadiene and is a rubbery material which can be obtained by polymerization using lithium butyl). The blend was then fed to an extruder which had a barrel extension capable of being heated to 450° C. The extension was maintained at 355° C. and the blend extruded through it at a contact time of 11 minutes. The resulting polymer was a soft flexible plastic having an inherent viscosity of 0.92, a stiffness of 11,000 psi. and a tensile strength of 1250 psi. It could be extruded into film, pipe or other shaped objects, and could be injection moulded into articles with improved toughness compared to conventional polyethylene.

70 When the temperature of the barrel extension was raised to 395° C., the product was a soft wax of low melt viscosity with greatly improved toughness. It could be coated onto paper by conventional wax coating equipment to give tough, flexible, moisture-resistant film which could be creased without cracking.

EXAMPLE 7

95 Polypropylene (1191.75 gms. I.V. 2.17, molecular weight 180,000, density 0.91) was blended by melting the polypropylene powder with polyethylene (397.25 gms. melt index 1.7, molecular weight 22,000, density 0.918) while stirring vigorously and the blend was then heated in a three-neck flask under nitrogen with stirring at 320—340° C. for approximately one and a half hours. The resulting product had an I.V. of 0.48, cloud point in paraffin of 97—98° C., and a melt viscosity of 14,000 cps. at 190° C. A mechanical blend (75/25 ratio) in which the amounts of the components are identical to that above containing degraded polypropylene (I.V. 0.45) and degraded polyethylene (I.V. approximately 4.49) had a cloud point in paraffin of 108—110° C. (The paraffin used for determining the closed point was Gulfwax, 130° F. melting point wax). The thermally modified wax obtained by the above process was coated on a roll of kraft paper from a melt at 190° C. and quenched rapidly with a chrome plated calendar roll. The resulting coating was tough and flexible and could be heat-sealed with conventional heat-sealing equipment. In contrast, paper coated from a mechanical blend of 75% polypropylene wax and 25% polyethylene wax gave a smooth coating, but this coating could not be heat-sealed satisfactorily due to embrittlement of the seal.

EXAMPLE 8

The same blend of polypropylene and polyethylene described in Example 7 was thermally modified as described in that Example by slowly heating to 365° C. and maintaining this temperature for 10 to 15 minutes. The resulting product had a melt viscosity of 2300 cps. and a cloud point of 93° C. It had useful wax properties and was more compatible than a simple blend which had approximately the same viscosity but which had a cloud point of 100—102° C.

EXAMPLE 9

Polypropylene (1509.5 gms. I.V. 2.17 molecular weight 180,000, density 0.91) was blended by melting the polypropylene powder with polyethylene (79.5 grams, melt index 1.7, molecular weight 22,000, density 0.918) while stirring vigorously and the blend was then heated in a three neck flask under nitrogen with stirring at 320—350° C. for one and three quarter hours. The resulting new polymer had an I.V. of 0.47, cloud point in paraffin of 99—100° C. and a melt viscosity at 190° C. of 8600 cps. A similar mechanical blend (95/5 ratio) of polypropylene (I.V. 0.45) and polyethylene (I.V. 0.49) had a cloud point in paraffin of 110—112° C. (The paraffin used for determining the cloud point was Gulfwax, 130° F. melting point wax). The improved compatibility of the thermally modified wax allows coating of paper or paper board at lower temperatures to give products with improved surface hardness and gloss.

EXAMPLE 10

Polypropylene (1509.5 gms. I.V. 2.03 molecular weight 180,000, density 0.91) was blended with polyethylene (79.5 gms. melt index 1.7, molecular weight 22,000, density 0.918) to give a 95/5 ratio mixture. This mixture was thermally modified in the same manner as described in Example 7 at 340—375° C. for approximately 1 hour. The resulting new product had an I.V. of 0.34 and a melt viscosity of 2700 cps. at 190° C. The cloud point of this thermally modified material was 91° C. which was much lower than that obtained (105° C.) from a comparable mechanical blend of the same viscosity.

EXAMPLE 11

Polypropylene (1350.6 gms. I.V. 2.17 molecular weight 180,000, density 0.91) was blended by melting the polypropylene powder with polyethylene (238.4 gms. melt index 1.7, molecular weight 22,000, density 0.918) while stirring vigorously to make an 85/15 ratio blend and the blend was then heated in a three-neck flask under nitrogen with stirring at 310 to 350° C. for 1 hour. The resulting product had a melt viscosity of 14,000 cps. at 190° C. and a cloud point of 101—102° C. A similar blend of polypropylene and poly-

ethylene of comparable viscosity made by simply blending had a much higher cloud point (115—116° C.) showing its lower degree of compatibility.

EXAMPLE 12

Polypropylene (1350.6 gms. I.V. 2.02 molecular weight 180,000, density 0.91) was blended by melting the polypropylene powder with polyethylene (238.4 gms. melt index 1.7, molecular weight 22,000, density 0.918) while stirring vigorously to give an 85/15 ratio mixture. This mixture was then heated in a three-neck flask under nitrogen with stirring at 370° C. for approximately 1 hour. The resulting product had an I.V. of 0.28 and a melt viscosity of 3400 cps. at 190° C. The cloud point of this thermally modified polymer was 93° C. The polymer had excellent wax properties and could be blended with paraffin wax to give compatible mixtures.

EXAMPLE 13

Polypropylene (350 gms. I.V. 3.0 molecular weight 270,000, density 0.92) was blended with polyethylene (150 gms. I.V. 1.3, molecular weight 38,000, density 0.91) yielding a blended material containing 30% polyethylene and 70% propylene. For comparison purposes, a copolymer was made (I.V. 1.6) containing 30% ethylene and 70% propylene. A portion of the mechanically blended polyethylene and polypropylene (30/70 ratio) was thermally modified at 295° C. for 20 minutes while stirring in a 1000 cc. three-neck flask under 1 mm. pressure. A very small amount of low boiling material was removed during this operation. The resulting thermally modified material had an I.V. of 1.8. The data in Table 4 shows clearly the difference in the properties of the thermally modified polymer as compared with blends and copolymers of the same over-all chemical composition. The simple mechanical blend has lower stiffness, tensile strength, elongation, and less transparency than the thermally modified resin. A copolymer of the same ratio, 30% ethylene and 70% propylene, has much lower stiffness, tensile strength, and transparency than the mechanical blend, or the thermally modified polymer.

The desirable combination of properties found in the thermally modified polymer such as high stiffness combined with high tensile strength and high elongation and good transparency makes it an ideal material for film production. This combination of high elongation with high stiffness, high tensile strength, and good transparency is found in the thermally modified material and is not found in the simple blends and copolymers.

EXAMPLE 14

One hundred forty grams of polyethylene (molecular weight 22,000, density 0.918) and

60 gms. of polymethyl methacrylate (molecular weight 100,000, density 1.18) were heated to 285° C. over a period of about 2 hours under nitrogen. The temperature was then gradually increased to 325° C. and held at this temperature for 3 hours. Some monomeric materials distilled out of the molten polymer. The molecular weight of the resulting polymer was 8,100. Oxygen analysis indicated 1.29% oxygen. This crude material was dissolved in hot benzene and then precipitated with acetone and washed repeatedly with hot acetone to remove any uncombined methyl methacrylate. This operation was continued until the wash acetone contained no soluble polymer. Approximately 50 gms. of this thermally modified polymer containing approximately 1% oxygen was then dissolved in hot benzene on the steam bath. To this solution was added 125 cc. of methyl alcohol. Twenty-five grams of KOH dissolved in an additional 125 cc. of methyl alcohol was then added producing a milky solution which was heated on the steam bath for approximately 1½ hours, then diluted with water and allowed to stand overnight. The material was decanted, washed with more water then acidified and heated on the steam bath. The product was then filtered and washed free of HCl. The new thermally modified polymer was then melted and titrated. It was found to have an acid number of 4.09, penetration hardness of 1½ on 100 gm.-scale for 5 sec. or 4½ on 200 gm.-scale for 5 sec. This material could be emulsified in water by the usual emulsification technique and was suitable for use as floor polish.

A mechanical blend similar to that above was prepared by mixing 140 gms. of thermally degraded polyethylene, molecular weight approximately 8000, with 60 gms. of polymethacrylate. The mixture was then heated to 185–210° C. with stirring until a uniform mixture was obtained. At this temperature the resulting product was essentially a mechanical mixture which was demonstrated by the fact that the two components could be completely separated by the process of dissolving in hot benzene and precipitation with acetone as described in Example 14 above. The acetone insoluble fraction gave a material with an acid number of zero after carrying out the hydrolysis step as described above indicating a non-emulsifiable wax as contrasted with the emulsifiable wax obtained by thermal treatment.

A copolymer of ethylene and methyl methacrylate was prepared of approximately the same overall-composition as that of the thermally modified polymer and polymethyl methacrylate. It was hydrolyzed in the same manner as described above to an acid number of 4.2. It formed a poor emulsion and was much softer (penetration of 1.5 on 100 gm.-scale for 5 sec.) than the thermally modified material. Thus, the thermally modified material was superior in emulsification and penetration hard-

ness to a copolymer of the same over-all composition.

EXAMPLE 15

In a similar procedure to that described in Example 14, 1000 gms. of polyethylene (molecular weight 22,000, density 0.918) was heated with 500 gms. of polyvinyl acetate (molecular weight 50,000, density 1.1) and blended to give a uniform mechanical blend which was then heated to 300° C. for one and a half hours with stirring under nitrogen. The resulting wax product was coated onto paper by the conventional hot melt process to give a tough, flexible, high gloss film which could be heat sealed without embrittlement. A simple mechanical mixture of pure polyethylene and the same polyvinyl acetate was found to separate out into two phases after standing in the melted state which rendered it unsuitable for this use. The thermally modified material was also found to adhere to the paper better than on unmodified polyether. The thin film coating of thermally modified polymer was tough and had improved grease retention when compared to a similarly coated polyethylene paper. This was determined by a modification of Army JAN-B-121 test (described in U.S. Federal Specification JAN-B-121) in which turpentine as well as cotton seed oil was used as the test liquid on creased paper.

Other polyvinyl esters such as polyvinyl methoxy acetate and polyvinyl stearate can also be used to prepare similar polymers. These materials also have excellent paper coating properties. The special properties of adherence, grease retention and heat sealability for the thermally modified polymers of this invention are superior to those obtained with polyethylene alone or with mechanical blends of polyethylene and these vinyl polymers.

EXAMPLE 16

Five hundred grams of polyvinyl 2 - ethylhexyl ether was blended with 500 gms. of polyethylene (molecular weight 22,000, density 0.918). This mechanical blend was heated with stirring to 300° C. for 2 hours. The product was a uniform polymeric material that could be coated onto paper by the conventional hot melt process to give a film that had excellent heat sealing properties. The wax coating could not be separated from the paper as can be done when polyethylene alone is used as the coating material.

Similar runs using polyvinyl 2 - methoxyethyl ether and polyvinyl 2 - chloroethyl ether instead of the polyvinyl 2 - ethylhexyl ether in the thermal treatment also produced excellent coating materials that had excellent adhesion to the paper.

EXAMPLE 17

Polyethylene (400 gms. of molecular weight 22,000 and density 0.918) was thermally modified with 100 gms. of polymer obtained by polymerizing diethyl methylene malonate. The

thermal treatment or modification was in the 275—300° C. range for 40 minutes under nitrogen. The new thermally created polymer was then spun into fibres. These fibres were found to be dyeable by regular dispersed type dyes such as 4 - (4' - β - hydroxyethyl anilino) - 5 - nitro - 1, 8 - dihydroxyanthraquinone. Thin films could also be printed when made from this thermally modified material.

EXAMPLE 18

A thermally modified polymer was obtained from polyethylene (49.5 gms. Tenite 800) ("Tenite" is a Trade Mark) and 5.0 gms. polymeric diethyl itaconate by heating in the 290—300° C. range for 30 minutes. The new product showed improved dyeing properties when compared with similarly treated polyethylene alone. (Tenite 800 is polyethylene of molecular weight 22,000, density 0.918, melt index 1.7 manufactured by Texas Eastman Company).

EXAMPLE 19

In like manner 425 gms. polyethylene molecular weight 22,000, density 0.918) and 75 gms of poly *n* - butyl acrylate (a polymer of *n* - butyl acrylate) were thermally modified by heating at 285—310° C. for 45 minutes. The thermally modified polymer had improved dyeing properties when compared with similarly treated polyethylene alone.

EXAMPLE 20

A copolymer of vinyl acetate and vinyl benzoate was prepared and then blended with polyethylene (molecular weight 22,000, density 0.918) in a 25—75 weight ratio there were 75 parts of polyethylene in the blend) and heated within a 280—350° C. range for 30 minutes under nitrogen. The new product was homogeneous, did not separate on melting, and showed improved dye absorption when compared with conventional polyethylene fibres and films.

Conditioned density, as used in the above examples, refers to the density determined on a sample which has been annealed in an attempt to obtain maximum crystallinity. A conventional annealing procedure involves placing the sample in a tube, heating under high vacuum or in a nitrogen atmosphere to just below the softening point and allowing the sample to cool slowly.

The unusual combination of physical characteristics possessed by the thermally created products embodying the invention is shown by the data summarized in Tables 2, 3 and 4 which follow. From an examination of this data it is obvious that the polymeric products obtained by the method of the present invention have characteristics which are different from and superior in many respects to the polyethylene products now available.

TABLE 2

	Tensile Yield Strength	Elongation	Izod Impact —40° C.	Stiffness Modulus
Polyethylene	1,450	595%	0.57	16,000 psi.
80% Polyethylene 20% Polyhexene-1 (blend)	1,235	125%	0.23	12,000 psi.
80% Polyethylene 20% polyhexene-1 (thermally modified)	1,350	700%	0.98	19,000 psi.

The data in the above table clearly illustrates the difference between the properties of the thermally modified ethylene polymers and those of the blends of the same overall-chemi-

cal composition. The simple mechanical blend has lower stiffness, tensile strength, impact strength and elongation than the thermally modified resins.

TABLE 3

	Stiffness Modulus	Tensile Yield Strength	Elongation	Film Transparency
Polyethylene	18,000 psi.	1,500	560%	60 in.
Blend 90% poly- ethylene and 10% copolymer, 4% butene-1 and 96% ethylene	20,000 psi.	1,560	160%	10 in.
Thermally modified 90% polyethylene and 10% copolymer, 4% butene-1 and 96% ethylene	21,000 psi.	1,520	620%	140 in.

TABLE 4

	Stiffness Modulus Psi.	Tensile Strength	Elongation %	Transparency In.
Blend 30% poly- ethylene 70% polypropylene	95,000 psi.	3200	76	10
Copolymer 30% ethylene 70% propylene	5,000 psi.	1100	700	50
Thermally modified blend 30% poly- ethylene 70% polypropylene	110,000 psi.	3600	550	170

Thus, by means of this invention, it is possible to "customize" or "tailor" polyethylene for a specific use by merely making a judicious choice of modifier. By the method of this invention it is possible to improve one or more of the characteristics of polyethylene to increase its value and versatility. Hence, ethylene polymers hitherto available can be improved in one or more characteristics such as grease and oil resistance, dyeability of fibres, printability of films, heat sealing properties in wax formulations, adhesion to paper, clarity, tensile strength, elongation, penetration hardness of a wax, compatibility and the like. The improved polymers can, of course, be substituted for conventional polyethylene whenever these improved properties are of significance. For example, because of the need for heat sealing in many packaging applications, the thermally modified waxes made by the method of the present invention are excellent substitutes for polyethylene now used, since the coating obtained therefrom combines the high strength, toughness, hardness, flexibility, and imperme-

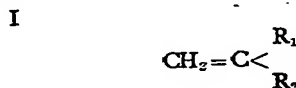
ability of the conventional polyethylene coatings with the ability to be heat sealed.

WHAT WE CLAIM IS:—

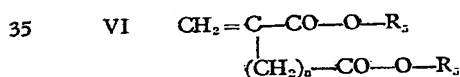
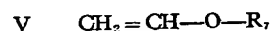
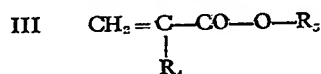
1. The method of modifying the properties of polyethylene which comprises heating at a temperature of at least 260° C., for at least one minute, a mixture of polyethylene having a density of at least 0.91 and a molecular weight of at least 10,000, with an amount from one-twentieth to nineteen times its weight of a modifier which consists of at least one homopolymer or copolymer derived from one or more polymerizable organic compounds containing, or each containing, at least one $\text{CH}_2=\text{C}<$ group, other than ethylene alone whereby the temperature and time of heating are sufficient to degrade the polyethylene and effect reaction between the polyethylene and the modifier.

2. The method of modifying the properties of polyethylene which comprises heating at a temperature of at least 260° C., for at least one minute, a mixture of polyethylene having a density of at least 0.91 and a molecular

- weight of at least 10,000, with an amount from one-twentieth to nineteen times its weight of a modifier which consists of at least one homopolymer or copolymer derived from one or more polymerizable organic compounds of the general formula:



- wherein either R_1 represents a methyl group, and
 10 R_2 represents an aliphatic, ethylenically unsaturated aliphatic or aromatic hydrocarbon radical containing from 1 to 20 carbon atoms, or
 15 R_1 and R_2 together represent the group $=\text{CH}_2$ or $=\text{CHR}$, where R is an alkyl group whereby the temperature and time of heating are sufficient to degrade the polyethylene and effect reaction between the polyethylene and the modifier.
 20 3. The method of modifying the properties of polyethylene which comprises heating at a temperature of at least 260°C , for at least one minute, a mixture of polyethylene having a density of at least 0.91 and a molecular weight of at least 10,000, with an amount from one-twentieth to nineteen times its weight of a modifier which consists of at least one homopolymer or copolymer derived from one or more unsaturated polymerizable organic compounds of any of the general formulae:—



wherein

- R_3 represents an aliphatic, ethylenically unsaturated aliphatic or aromatic hydrocarbon radical containing from 1 to 20 carbon atoms,
 40 R_4 represents a hydrogen atom or a methyl group,

R_5 represents an alkyl group containing from 1 to 8 carbon atoms,

R_6 represents a hydrogen atom, an aryl group, a methyl group, a halogenomethyl group or an alkoxymethyl group in which the alkoxyl radical contains from 1 to 8 carbon atoms,

R_7 represents an alkyl group containing from 1 to 8 carbon atoms, an alkenyl or aralkenyl group containing from 1 to 8 carbon atoms, an alkoxyalkyl group containing from 1 to 8 carbon atoms in its alkyl and alkylene residues or a halogenoalkyl group containing from 1 to 8 carbon atoms, and

n represents 0 or 1 whereby the temperature and time of heating are sufficient to degrade the polyethylene and effect reaction between the polyethylene and the modifier.

4. The method as claimed in any of claims 1 to 3 in which the heating is carried out at a temperature within the range 260° to 450°C .

5. The method as claimed in claim 4 in which the heating is carried out at a temperature within the range 290° to 400°C .

6. The method as claimed in any of the preceding claims in which the time of heating does not exceed 4 hours.

7. The method as claimed in any of the preceding claims in which the heating is carried out in the absence of air.

8. The method as claimed in any of claims 1 or 3 to 7 wherein the modifier is polypropylene.

9. The method as claimed in any of claims 1 or 3 to 7 wherein the modifier is polystyrene.

10. The method as claimed in any of claims 1 or 3 to 7 wherein the modifier is polymethyl methacrylate.

11. The method as claimed in any of claims 1 or 3 to 7 wherein the modifier is poly-3-methylbutene-1.

12. The method as claimed in any of claims 1 or 3 to 7 wherein the modifier is a copolymer of 4% butene-1 with 96% ethylene, by weight.

13. The method as claimed in claim 1 of modifying the properties of polyethylene and the modified polyethylene so obtained, as herein particularly described and illustrated by the Examples.

14. The modified polyethylene obtained by the method as claimed in any of the preceding claims.

15. A wax, coating, fibre or film formed from the modified polyethylene of claim 14.

W. P. THOMPSON & CO.,
 12 Church Street, Liverpool, 1.
 Chartered Patent Agents.